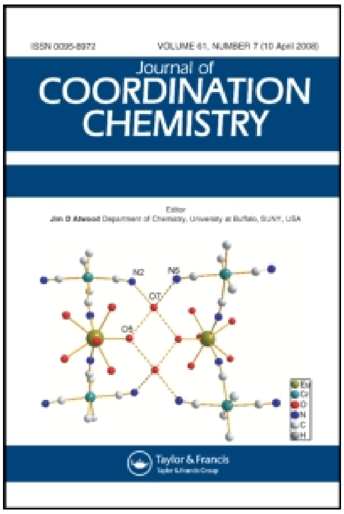

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TRIPLE INSERTION OF ETHYLISOCYANATE INTO A W–Cl BOND AND ITS INNER-SPHERE CYCLIZATION. CRYSTAL STRUCTURE OF TETRACHLOROOXO (3,5-DIETHYL-2-METHYLAMINO[1,3,5]-OXADIAZINE-2,4-DIONE)TUNGSTEN(VI)

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The insertion product $[WCl_5\{N(Et)C(O)OC(NEt)N(Et)C(O)Cl\}]$ (**I**) is obtained by the room-temperature reaction of WCl_6 with an excess of EtNCO in dichloroethane. The structure of the chain ligand in **I** is deduced from an IR study and the results of X-ray diffraction analyses of crystals of an oxo-complex, $WOCl_4\{O\overline{CN(Et)C(O)N(Et)C(NHEt)O}\}$(**II**), which is obtained by partial hydrolysis of **I**.

Keywords: Tungsten hexachloride; Complexes; Insertion reaction; Cyclization; Ethylisocyanate; Crystal structure

INTRODUCTION

Unsaturated compounds can be coordinated with transition metal ions in several ways, and this allows their attachment to a metal–ligand bond. Moreover, it allows the design of complex organic molecules by formation of a chain of inserted molecules, followed by cyclization when they are removed from the coordination sphere. This allows synthesis of known compounds under milder conditions as well as building new organic compounds, especially heterocycles, which have great practical importance.

The insertion of organic isocyanate and isothiocyanate into the M–O bond (M = Nb, Ta) has been described before [1,2]. Using the reactions of halides of the Group V transition metals, we have found that RNCO (R = Me, Et) will insert into the M–Hal bond [3]. Remarkably, some of those reactions involved the attachment of

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several ligands into one M–L bond [4,5]. Gibson and co-workers reported selective insertion of PhNCO into two Mo–O bonds of $Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)_2(O\text{-}Bu^t)_2$, while RNCS added to only one of the M–N bonds [6].

Recently we established that ethylisocyanate can be attached to the tungsten–chlorine bond by refluxing in dichloroethane [7]. Hydrolysis of this compound leads to the formation of a derivative of symmetrical triazine that indicates the presence of a chain in the insertion product, which consists of three isocyanate fragments inserted into one W–Cl bond and connected to each other by C–N bonds.

It was interesting to attempt insertion of the ethylisocyanate into tungsten hexachloride in dichloroethane media under mild conditions, and to carry out a comparative analysis with available data. In the case of the formation of crystalline of products, their stereochemistry was investigated by X-ray structure analysis.

EXPERIMENTAL

In our experiments we used WCl_6 purified by vacuum distillation and ethylisocyanate supplied by Fluka, GmbH. Dichloroethane was purified and dried by standard methods. The reaction was performed in dry argon. When reaction was complete the precipitates were separated from the mother liquid by decanting, washed several times with carbon tetrachloride, and dried *in vacuo* to a constant weight.

Hydrogen, carbon and nitrogen were determined by a Carlo Erba EA 1108 C,H,N,S microanalyzer. Analysis for chlorine was performed by the Volhard method (after alkaline decomposition of samples).

The IR absorption spectra were recorded by a Specord 75 IR in the range of 4000–400 cm^{-1} (Nujol, KBr).

Preparation of the Compounds

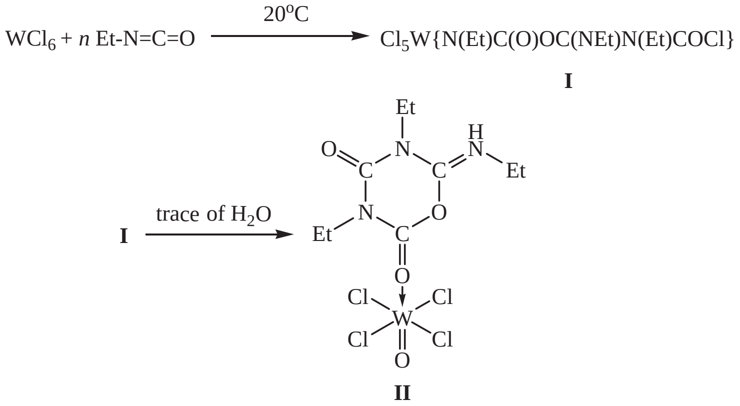
$[WCl_5\{N(Et)C(O)OC(NEt)N(Et)C(O)Cl\}]$ (I)

A solution of EtNCO (1.06 mL, 13.48 mmol) in 5 mL of dichloroethane was added dropwise to a suspension of WCl_6 (1.78 g, 4.49 mmol) in 20 mL of dichloroethane at room temperature (21°C). The color of the solution changed from orange to brown. The volume was reduced by two thirds under vacuum and crystals of **I** were obtained as red-brown, diamagnetic, highly hygroscopic prisms. Yield: 80%. Anal. Calcd. for $WCl_6C_9H_{15}N_3O_3$(%): N, 6.89; C, 17.73; H, 2.48; Cl, 34.88. Found: N, 6.25; C, 18.18; H. 2.77; Cl, 33.73. IR (KBr, Nujol): 1776 (st), 1722 (vs), 1570 (vs), 1312 (m), 1200 (m), 1116 (m), 1080 (st), 1022 (m), 956 (vs), 746 (vs), 495 (st), 478 (m) cm^{-1}.

Crystals of **I** were decomposed by X-ray radiation so we were unable to determine their structure.

$WOCl_4\{\overline{OCN(Et)C(O)N(Et)C(NHEt)O}\}(II)$

A solution of EtNCO (0.7500 mL, 9.538 7 mmol) in 5 mL of dichloroethane was added dropwise to a suspension of WCl_6 (1.8805 g, 4.7419 mmol) in 20 mL of dichloroethane at room temperature (21°C). After two months black brown crystals of **II** separated out of solution. Yield: 80%. The composition and structure of the crystals were established



Scheme I

TABLE I Crystal data and experimental parameters for **II**

Formula	$C_9H_{16}Cl_4N_3O_4W$
Formula weight	555.89
Crystal system	Triclinic
a (Å)	8.8120(7)
b (Å)	9.8564(8)
c (Å)	9.8669(8)
α (°)	87.009(2)
β (°)	81.624(2)
γ (°)	85.323(2)
V (Å)^3	844.3(1)
$D_{\text{calc.}}$ (g cm^{-3})	2.183
μ_{Mo} (cm^{-1})	74.89
Z	2
Space group	P-1
F (000)	528
$2\theta_{\max}$ (°)	60
Index range	$-12 \le h \le 9$; $-13 \le k \le 3$;$13 \le l \le 12$
Total no. of reflns	4418
No. of reflns with $I \ge 2\sigma(I)$	3186
R(int)	0.032
$R1$, $wR2$ ($I \ge 2\sigma(I)$)	0.087, 0.229
$R1$, $wR2$ (for all reflns)	0.097, 0.240
Goodness of fit	1.069
No. of variables	116
$\Delta\rho$(max), $\Delta\rho$(min), e/Å^3	5.099, −4.324

by X-ray diffraction. IR (KBr, Nujol): 3186 (m), 1800 (m), 1734 (vs), 1674 (vs), 1510 (l), 1326 (m), 1124 (m), 1070 (m), 992 (s), 726 (m), 436 (m) cm^{-1}.

X-ray Crystallography

Intensity data for Compound **II** were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$Å). Crystals of Complex **II**, which are unstable in air, were placed in a capillary.

The structure was solved by direct methods [8] and refined with the full-matrix least squares technique [9], anisotropically for W and isotropically for all other non-hydrogen atoms.

TABLE II Atomic coordinates per axial fractions of the unit cell and thermal corrections *U*(iso)/*U*(eq) for **II**

Atom[a]	*x*	*y*	*z*	*U*(iso)/*U*(eq) (Å^2)
W(1)	0.8101(1)	0.7375(1)	0.7702(1)	0.0246(3)
Cl(1)	0.9938(6)	0.8591(4)	0.6154(4)	0.017(2)
Cl(2)	0.8008(6)	0.5928(4)	0.5875(4)	0.017(2)
Cl(3)	0.916(1)	0.8450(8)	0.9452(8)	0.035(2)
Cl(4)	0.7064(7)	0.5662(8)	0.9256(5)	0.029(2)
O(1)	1.0450(8)	0.5936(7)	0.7850(7)	0.013(1)
O(2)	1.4534(9)	0.2876(8)	0.7001(8)	0.022(2)
O(3)	1.0095(8)	0.3774(7)	0.7613(7)	0.012(1)
O(4)	0.6552(8)	0.8448(8)	0.7596(9)	0.024(2)
N(1)	1.255(1)	0.4478(9)	0.7436(9)	0.026(2)
N(2)	1.213(1)	0.2186(9)	0.712(1)	0.031(2)
N(3)	0.959(1)	0.1661(9)	0.7280(9)	0.025(2)
C(1)	1.104(1)	0.480(1)	0.764(1)	0.013(2)
C(2)	1.361(1)	0.558(1)	0.746(1)	0.019(2)
C(3)	1.375(1)	0.643(1)	0.611(1)	0.023(3)
C(4)	1.319(1)	0.314(1)	0.719(1)	0.015(2)
C(5)	1.274(2)	0.083(2)	0.651(2)	0.003(5)
C(6)	1.296(2)	−0.013(2)	0.778(2)	0.008(6)
C(5A)	1.283(2)	0.071(2)	0.720(2)	0.019(6)
C(6A)	1.337(3)	0.035(2)	0.577(3)	0.034(7)
C(7)	1.060(1)	0.249(1)	0.734(1)	0.012(2)
C(8)	0.788(1)	0.207(1)	0.749(1)	0.020(2)
C(9)	0.719(1)	0.192(1)	0.895(1)	0.028(3)
Cl(1A)	0.961(5)	0.861(2)	0.614(2)	0.13(1)
Cl(2A)	0.771(4)	0.597(2)	0.596(3)	0.12(1)
Cl(3A)	0.891(2)	0.825(1)	0.959(1)	0.041(4)
Cl(4A)	0.687(2)	0.596(3)	0.930(2)	0.071(5)
H(N3)	0.988	0.083	0.712	0.08
H(21)	1.460	0.518	0.760	0.08
H(22)	1.322	0.616	0.820	0.08
H(31)	1.443	0.712	0.614	0.08
H(32)	1.415	0.585	0.536	0.08
H(33)	1.275	0.683	0.596	0.08
H(51)	1.369	0.091	0.591	0.08
H(52)	1.201	0.050	0.599	0.08
H(61)	1.334	−0.102	0.747	0.08
H(62)	1.368	0.022	0.828	0.08
H(63)	1.199	−0.019	0.836	0.08
H(51A)	1.206	0.011	0.762	0.08
H(52A)	1.366	0.063	0.772	0.08
H(61A)	1.382	−0.056	0.575	0.08
H(62A)	1.251	0.043	0.526	0.08
H(63A)	1.412	0.095	0.537	0.08
H(81)	0.737	0.152	0.964	0.08
H(82)	0.771	0.300	0.717	0.08
H(91)	0.610	0.219	0.903	0.08
H(92)	0.733	0.098	0.926	0.08
H(93)	0.767	0.248	0.949	0.08

[a] Atomic OF is equal to 0.65(3) for Cl(1)–C(4), C(5), C(6), and 0.35(4) for Cl(1A)–Cl(4A), C(5A), C(6A).

The positions of hydrogen atoms were geometrically calculated (C–H 0.96, N–H 0.90 Å); and H atoms in fixed positions were included in the final structure refinement. In structure **II** all chlorine atoms were disordered in two positions (Cl(*n*) and Cl(*n*A), $n = 1$–4). Chlorine atoms of the same name (of two orientations) of molecule **II** are offset at 0.27(3)–0.33(3) Å. Carbon atoms of one of the ethyl groups of the organic ligand L are also statistically disordered; distances are C(5)–C(5A) = 0.71(3), and C(6)–C(6A) = 0.99(3) Å. The occupancy factors (OF) of disordered atoms were refined

TABLE III Bond length (*d*) and angles (*w*) for **II**

Bond	*d* (Å)	*Bond*	*d* (Å)
W(1)–Cl(1)	2.407(5)	W(1)–Cl(2)	2.371(4)
W(1)–Cl(3)	2.386(8)	W(1)–Cl(4)	2.368(7)
W(1)–O(1)	2.430(7)	W(1)–O(4)	1.674(7)
W(1)–Cl(1A)	2.26(3)	W(1)–Cl(2A)	2.34(3)
W(1)–Cl(3A)	2.32(2)	W(1)–Cl(4A)	2.26(2)
O(1)–C(1)	1.21(1)	O(3)–C(1)	1.36(1)
O(2)–C(4)	1.18(1)	N(1)–C(1)	1.33(1)
O(3)–C(7)	1.34(1)	N(1)–C(4)	1.41(1)
N(1)–C(2)	1.49(1)	N(2)–C(5)	1.52(2)
N(2)–C(4)	1.38(1)	N(2)–C(7)	1.35(1)
N(2)–C(5A)	1.54(2)	N(3)–C(8)	1.51(1)
N(3)–C(7)	1.26(1)	C(5)–C(6)	1.56(3)
C(2)–C(3)	1.53(2)	C(8)–C(9)	1.49(2)
C(5A)–C(6A)	1.47(4)		
Angle	*w* (°)	*Angle*	*w* (°)
Cl(1)–W(1)–Cl(2)	86.9(2)	Cl(1)–W(1)–Cl(3)	84.6(2)
Cl(1)–W(1)–Cl(2)	160.1(2)	Cl(1)–W(1)–O(1)	78.8(2)
Cl(1)–W(1)–O(4)	97.9(3)	Cl(2)–W(1)–O(1)	80.7(2)
Cl(2)–W(1)–Cl(4)	88.9(2)	Cl(2)–W(1)–Cl(3)	157.9(2)
Cl(2)–W(1)–O(4)	100.7(3)	Cl(3)–W(1)–Cl(4)	92.2(3)
Cl(3)–W(1)–O(1)	77.8(3)	Cl(3)–W(1)–O(4)	100.6(3)
Cl(4)–W(1)–O(1)	81.4(2)	Cl(4)–W(1)–O(4)	102.0(3)
O(1)–W(1)–O(4)	176.4(3)	O(1)–W(1)–Cl(1A)	84.3(8)
O(1)–W(1)–Cl(2A)	86.1(7)	O(1)–W(1)–Cl(3A)	79.5(4)
O(1)–W(1)–Cl(4A)	88.2(6)	O(4)–W(1)–Cl(1A)	92.4(8)
O(4)–W(1)–Cl(2A)	95.5(8)	O(4)–W(1)–Cl(3A)	99.2(5)
O(4)–W(1)–Cl(4A)	95.0(6)	Cl(1A)–W(1)–Cl(2A)	89(1)
Cl(1A)–W(1)–Cl(3A)	94.9(9)	Cl(1A)–W(1)–Cl(4A)	172.5(9)
Cl(2A)–W(1)–Cl(3A)	164.4(8)	Cl(2A)–W(1)–Cl(4A)	90.4(9)
C(1)–O(3)–C(7)	124.0(8)	Cl(3A)–W(1)–Cl(4A)	83.4(7)
C(1)–N(1)–C(4)	122.6(9)	C(1)–N(1)–C(2)	118.7(9)
C(4)–N(2)–C(5)	117(1)	C(2)–N(1)–C(4)	118.7(8)
C(4)–N(2)–C(7)	123.3(9)	C(4)–N(2)–C(5A)	113(1)
C(7)–N(3)–C(8)	123.0(9)	C(5)–N(2)–C(7)	118(1)
O(1)–C(1)–N(1)	124(1)	O(1)–C(1)–O(3)	118.0(9)
N(1)–C(2)–C(3)	111.0(9)	O(3)–C(1)–N(1)	117.6(9)
O(2)–C(4)–N(2)	123(1)	O(2)–C(4)–N(1)	121(1)
N(2)–C(5)–C(6)	104(2)	N(1)–C(4)–N(2)	115.1(9)
O(3)–C(7)–N(2)	117.4(9)	N(2)–C(5A)–C(6A)	105(3)
N(2)–C(7)–N(3)	126(1)	O(3)–C(7)–N(3)	117.0(9)
		N(3)–C(8)–C(9)	112.1(9)

and the OF for Cl(1)–Cl(4), C(5), C(6) atoms was 0.65(3) and for Cl(1A)–Cl(4A), C(5A), C(6A) = 0.35(4). Crystal data, data collection, and least squares parameters are listed in Table I. The coordinates and thermal parameter factors $U(\mathrm{eq})/U(\mathrm{iso})$ of atoms in the structure are given in Table II, bond lengths and angles are given in Table III.

RESULTS AND DISCUSSION

The interaction of WCl_6 with an excess of EtNCO in dichloroethane at room temperature results in insertion of three molecules of EtNCO into the W–Cl bond giving $[WCl_5\{(EtNCO)_3Cl\}]$ (**I**). The IR spectrum of **I** shows three bands corresponding to the ν(C=O) and ν(C=N) vibrations in the region of 1780–1550 cm^{-1} and a single band ν(C–Cl) (746 cm^{-1}), indicating the chain character of the addition of the inserted fragments.

Despite the identical composition of the chain ligand in **I** with its analog obtained under high-temperature synthesis **III** [7], the differences in the IR spectra (in the region of 1750–1590 cm^{-1}) allow us to interpret various bonding isomers of chained ligand in these compounds.

X-ray diffraction data for $WOCl_4\{\overline{OCN(Et)C(O)N(Et)C(NHEt)O}\}$(**II**) the product of particular hydrolyses of **I**, support our assumption that the fragments in the cyclic ligand of **II** are bonded by bonds of both kinds (namely, by C–N and C–O bonds), in contrast to a symmetrical insertion of the isocyanate (by three C–N bonds), which is produced by refluxing WCl_6 and EtNCO in dichloroethane [7]. The 1,3,5-oxadiazinic ligand in **II** can be explained by cyclization of the isocyanate chain from hydrolysis of both the primary insertion product **I** (see Scheme I).

Apart from this observation, there is only one known example of asymmetric condensation of isocyanate [10].

The change of temperature of both the reaction mixture leads to intra-molecular rearrangement of the chain of both the inserted molecules and the structural orderliness.

Crystal Structure of Complex II

The X-ray structural determination confirmed that **II** is the complex molecule [$WOCl_4L$] (Fig. 1), where L is a derived 1,3,5-oxadiazinic ligand produced by condensation of three EtNCO molecules in the reaction of WCl_6 with EtNCO.

The coordination polyhedron of tungsten atoms is a distorted octahedron with four chlorine atoms, Cl(1)–Cl(4), in the equatorial plane, and an oxo-ligand in an axial site. The second axial site in the coordination octahedron of tungsten is occupied by an O(1) atom of the monodentate organic ligand (L). The tungsten atom is displaced from the equatorial plane towards the oxo-ligand by 0.428 Å (the equatorial Cl ligands are co-planar within ± 0.02 Å). The W=O(oxo) bond length (1.674(7) Å) is similar in length to those found in d^0-W(VI)-complexes (1.698 ± 0.012 Å [11] and 1.713 ± 0.037 Å [12]) for all 14 monomeric compounds in the former case, and for 12 monomeric octahedral complexes in the latter.

The bond length range for the W–Cl equatorial bonds in **II** is 2.368(7)–2.407(5) Å. In what follows we discuss only one of the two orientations of the disordered molecule $WOCl_4L$ with the Cl(1)–Cl(4) atoms (OF = 0.65). The average W–Cl (equ.) distance (2.383 ± 0.024 Å) falls in the wide interval of average values for W–Cl (equ.) bond distances in 16-ty W(VI) MOC (2.290–2.436 Å, 2.330 ± 0 .106 Å [12]).

The W–O(L)(*trans*) bond lengths (2.430(7) Å) are significantly longer than those found in 11 W(VI) compounds [12] (W–O(*trans*) bond length 2.12–2.39 Å).

The six-membered heterocycle N_2OC_3 of ligand L is essentially planar. The planarity of the heterocycle indicates delocalization of the electron density around the ring, and the plane coordination of sp^2-hybridized atoms C(1), C(4), C(7), N(1), N(2). For acyclic atom N(3) the distances, N(3)–C(7) 1.26(1) and N(3)–C(8) 1.51(1) Å are comparable to the accepted values for double and single bonds, respectively. As usual, the bond length C(1)–O(1) of the carbonyl group coordinated to tungsten is longer than the terminal carbonyl bond.

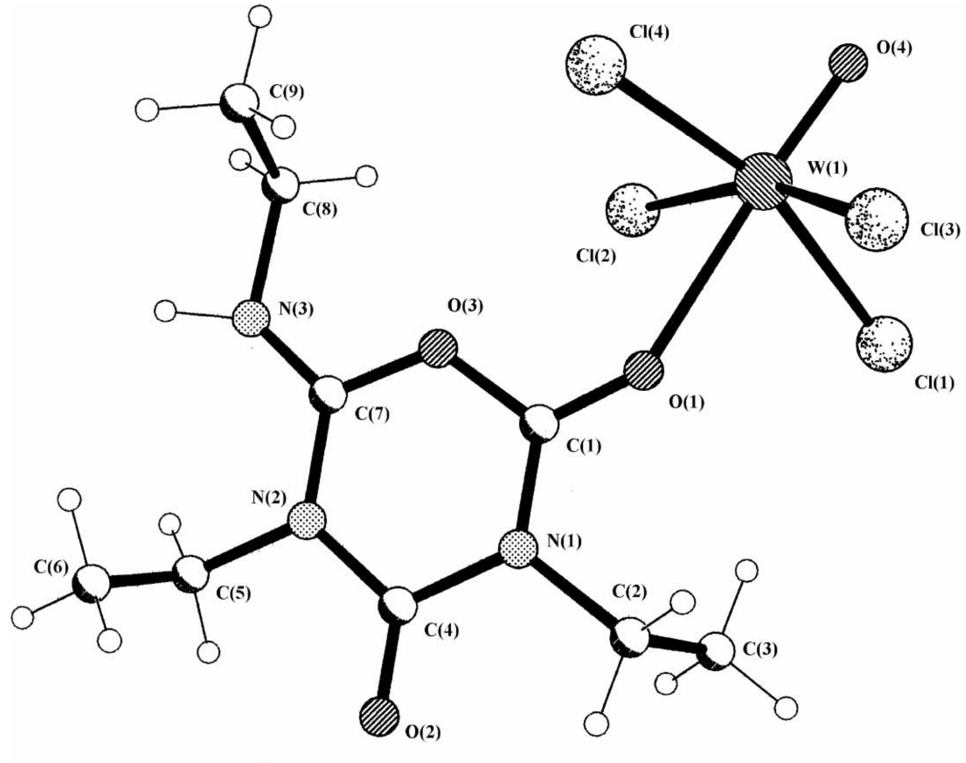


FIGURE 1 Structure of complex molecule $WOCl_4L$. Only one of two orientations of the molecule (with OF for atoms Cl(1)–Cl(4), C(5), C(6), equal to 0.65) is shown for clarity.

TABLE IV Short intermolecular interactions in **II**

Contact A–H···B *A···B*	*Position of atom B*	*Length* (Å)[a]		*Angle AHB* (°)
		A···B	*H···B*	
N(3)–H(N3)···Cl(1)	$x, -1+y, z$	3.253(9)	2.45	159
N(3)–H(N3)···Cl(1)	$2-x, 1-y, 1-z$	3.373(9)	3.23	92
C(2)–H(21)···Cl(4)	$2-x, 1-y, 2-z$	3.39(1)	2.97	109
C(3)–H(32)···O(2)	$3-x, 1-y, 1-z$	3.28(1)	2.74	116
C(5)–H(52)···Cl(1)	$x, -1+y, z$	3.51(2)	2.71	141
C(6)–H(62)···O(4)	$1+x, -1+y, z$	3.33(2)	2.97	104
C(6)–H(63)···Cl(3)	$2-x, 1-y, 2-z$	3.51(2)	2.88	125
C(8)–H(81)···O(2)	$-1+x, y, z$	3.09(1)	2.73	103
C(9)–H(91)···O(2)	$-1+x, y, z$	3.29(2)	2.63	126
Cl(1)···Cl(1)	$2-x, 2-y, 1-z$	3.498(5)		
Cl(2)···N(1)	$2-x, 1-y, 1-z$	3.42(1)		
Cl(2)···N(2)	$2-x, 1-y, 1-z$	3.42(1)		
Cl(1)···(5)	$x, 1+y, z$	3.51(2)		
Cl(2)···C(1)	$2-x, 1-y, 1-z$	3.54(1)		
Cl(2)···C(4)	$2-x, 1-y, 1-z$	3.40(1)		
Cl(2)···C(7)	$2-x, 1-y, 1-z$	3.56(1)		
Cl(3)···N(2)	$2-x, 1-y, 2-z$	3.44(1)		
Cl(3)···C(7)	$2-x, 1-y, 2-z$	3.28(1)		
Cl(4)···N(1)	$2-x, 1-y, 2-z$	3.33(1)		

[a] Fixed bond length: N–H 0.90, C–H 0.96 Å.

Table IV shows some selected intermolecular distances which are comparable with the sums of van der Waals radii (VWR) or with double values of VWR for corresponding atoms (H 1.16, C 1.71, N 1.50, O 1.29, Cl 1.90 Å [13]). The N–H group is involved in a strong hydrogen bond with the Cl atom of a neighbor, supplemented by a weak intermolecular interaction N–H···Cl with another molecule. In the crystal every molecule of **II** interacts with eight neighboring molecules.

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